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Improvements in the Solid Solution
Modeling Capabilities of the EQ3/6
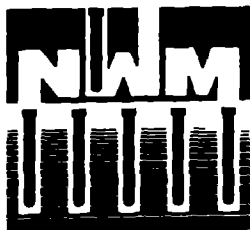Geochemical Code

William L. Bourcier

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Improvements in the Solid Solution Modeling Capabilities of the EQ3/6 Geochemical Code

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Introduction

This document describes modifications of EQ3NR and EQ6 extending their abilities to handle solid solution mineral phases in the calculations of aqueous speciation and in reaction pathway models. The codes handle solid solution phases in two ways. If the composition of the solid solution is given in the input file, the saturation state of that phase can be calculated. Alternatively, if only the composition of the aqueous phase is specified in the input file, the codes can determine the thermodynamically most stable composition of a solid solution and the corresponding saturation index. Thus, for example, the EQ6 code can now model an evolving fluid and continuously adjust the composition of the solid solution to maintain it in equilibrium with the fluid. This capability was not previously present in a reliable form. The subroutine HPSAT is called by both EQ3NR and EQ6 to handle the later, so called 'hypothetical solid solution problem'. Also, because the codes can now predict solid solution compositions when only solution compositions are input, they are better able to investigate whether solid solutions incorporating trace amounts of radionuclides are likely to act as solubility limiting phases for those radionuclides.

This report is organized as follows. The equations governing the thermodynamic treatment of solid solutions are first derived, followed by a brief discussion of the SIMPLEX algorithm used to solve the hypothetical solid solution problem. Some alternate algorithms used to solve the same problem and serve to verify the SIMPLEX method are also discussed. Limitations of the current code are then described along with planned changes to account for them. Finally, some present and future modifications of the solid solution data base are described.
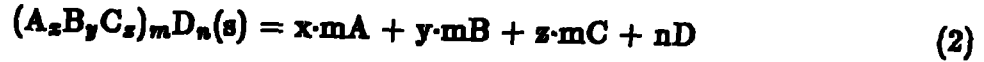
Solid Solution Model

The treatment discussed here should be termed a molecular mixing model of solid solutions, where solid solutions are treated as combinations of endmember minerals and therefore as functions of endmember thermodynamic properties (i.e. analogous to a solution of molecular species such as toluene and benzene).

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The saturation index (SI$_i$) for a pure phase is defined as:

$$SI_i = \log\left(\frac{Q_i}{K_i}\right) \tag{1}$$

where Q_i is the activity product, K_i the equilibrium constant for the mineral dissolution reaction, and here the activity of the solid phase assumed equal to unity.* For a dissolution reaction of a solid solution written as:

$$(A_x B_y C_z)_m D_n(s) = x \cdot mA + y \cdot mB + z \cdot mC + nD \tag{2}$$

the saturation index for the solid solution is defined:

$$SI_{ss} = \left(\frac{a_A^{xm} \cdot a_B^{ym} \cdot a_C^{zm} \cdot a_D^{n}}{a_{ss} \cdot K_{sp,ss}}\right) \tag{3}$$

where here a_{ss} and $K_{sp,ss}$ are the activity and solubility product, respectively, for the solid solution phase. If we choose as our standard state that $a_{ss}=1$ for all compositions, we can calculate the value for $K_{sp,ss}$ in terms of the K_{sp} values for the endmembers as follows. At equilibrium, both the solid solution phase and each endmember component are saturated. Thus for the phase $(A_x B_y C_z)_m D_n(s)$ having as endmember components $A_m D_n$, $B_m D_n$, and $C_m D_n$, at saturation the following relationships hold for the endmember components:

$$K_{sp,A_mD_n} = \left(\frac{a_A^m a_D^n}{a_{A_mD_1(s)}}\right) \tag{4}$$

$$K_{sp,B_mD_n} = \left(\frac{a_B^m a_D^n}{a_{B_mD_1(s)}}\right) \tag{5}$$

$$K_{sp,C_mD_n} = \left(\frac{a_C^m a_D^n}{a_{C_mD_1(s)}}\right) \tag{6}$$

Assuming here that $x+y+z=1$, the solubility product for $(A_x B_y C_z)_m D_n(s)$ can be written as:

$$K_{sp,ss} = a_A^{xm} a_B^{ym} a_C^{zm} a_D^{nx+ny+nz} \tag{7}$$

Because equations 4-6 are valid at equilibrium, we can substitute them into equation 7 giving:

$$K_{sp,ss} = (a_{A_mD_n} K_{sp,A_mD_n})^x (a_{B_mD_n} K_{sp,B_mD_n})^y (a_{C_mD_n} K_{sp,C_mD_n})^z \tag{8}$$

Finally, substitution of 8 into 3 and rearranging yields:

$$SI_{ss} = x \cdot \log\left(\frac{a_A^m a_D^n}{a_{A_mD_n} K_{sp,A_mD_n}}\right) + y \cdot \log\left(\frac{a_B^m a_D^n}{a_{B_mD_n} K_{sp,B_mD_n}}\right) + z \cdot \log\left(\frac{a_C^m a_D^n}{a_{C_mD_n} K_{sp,C_mD_n}}\right) \tag{9}$$

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* See section 2.3.6 of the EQ3NR Users Guide for further discussion of saturation indices.

where $a_{A_m D_n}$, $a_{B_m D_n}$, and $a_{C_m D_n}$ are the activities of the solid solution endmembers in the solid solution phase. For ideal mixing they are simply equal to their mole fractions. For non-ideal solid solutions the activities are given by:

$$a_l = \lambda_{(i,j,k..)} \cdot X_l \qquad (10)$$

where λ values are given by some function of the composition of the solid solution and are calculated using some experimental or theoretical mixing model.*

For the more general case of an n-component solid solution, equation 9 can be written as:

$$SI_{ss} = \sum_{l=1}^{n} X_l \cdot \log \left(\frac{Q_l}{K_l \cdot a_l} \right) \qquad (11)$$

which is the form of the equation programmed into subroutine HPSAT. In its present form, therefore, the subroutine deals only with so-called 'molecular mixtures' of endmember phases, and can not be used with minerals that mix over multiple sites. Work is in progress to derive an analog of equation 11 for more complex solid solutions that will allow mixing over multiple sites. Such a model will be described as a pseudo-site mixing model in that it will handle complex solid solutions which mix over multiple sites, such as clay and zeolite minerals, but would continue to model the solid solutions using thermodynamic properities of endmember components, as do molecular mixing models.

Equation 11 enables us to calculate the saturation index for a solid solution of given composition for any aqueous solution, given the activities of the relevant aqueous species, the solubility products of the endmember phases, and non-ideal mixing parameters for the non-ideal solid solutions. A related problem that is also encountered in geochemical modeling is that of determining, for a given aqueous system, what is the least soluble, and therefore thermodynamically most stable solid solution composition. In this case the composition of the solid solution phase is not known. Consider the problem encountered when one attempts to model an evolving fluid in equilibrium with some solid solution phase. Because the fluid is constantly changing composition, and the composition of the least soluble solid solution phase depends on the fluid composition, one must be able to determine the composition of the least soluble solid solution phase at each point along the reaction pathway. Mathematically, this is equivalent to finding the maximum of the saturation index defined by equation 11 above.

A simple analytical solution to the above problem for the case of ideal mixing, where $a_i = X_i$, can be obtained as follows. The maximum value for SI_{ss} can be determined by taking the partial derivatives of equation 11 with respect to all compositions, setting them equal to zero, and solving the resulting equations. Take the case of a three component solid solution having X_1, X_2, and X_3 as mole fractions of endmember phases. Equation 11 becomes:

$$SI_{ss} = X_1 \log \left(\frac{Q_1}{K_1 \cdot X_1} \right) + X_2 \log \left(\frac{Q_2}{K_2 \cdot X_2} \right) + X_3 \log \left(\frac{Q_3}{K_3 \cdot X_3} \right) \qquad (12)$$

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* See Table 3 of Wolery (1979) for a listing of solid solution models currently present in the codes.

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Noting that the mole fractions must sum to unity,

$$X_1 + X_2 + X_3 = 1 \tag{13}$$

substitution of 13 into 12 gives:

$$SI_{ss} = X_1 \log \left(\frac{Q_1}{K_1 \cdot X_1} \right) + X_2 \log \left(\frac{Q_2}{K_2 \cdot X_2} \right) + (1 - X_1 - X_2) \log \left(\frac{Q_3}{K_3 \cdot (1 - X_1 - X_2)} \right) \tag{14}$$

Now take the partial derivatives of 14 with respect to each composition variable. For X_1, the expression is:

$$\frac{\partial SI_{ss}}{\partial X_1} = X_1 \left(\frac{\partial \log \left(\frac{Q_1}{K_1 \cdot X_1} \right)}{\partial X_1} \right) + \log \frac{Q_1}{K_1 \cdot X_1} + (1 - X_1 - X_2) \left(\frac{\partial \log \left(\frac{Q_3}{K_3 \cdot (1 - X_1 - X_2)} \right)}{\partial X_1} \right)$$

$$- \log \frac{Q_3}{K_3 \cdot (1 - X_1 - X_2)} = 0 \tag{15}$$

which simplifies to:

$$\log \left(\frac{Q_1}{K_1 \cdot X_1} \right) = \log \left(\frac{Q_3}{K_3 \cdot X_3} \right) \tag{16}$$

Similarly, for the partial derivative with respect to X_2:

$$\log \left(\frac{Q_2}{K_2 \cdot X_2} \right) = \log \left(\frac{Q_3}{K_3 \cdot X_3} \right) \tag{17}$$

By combining equations 16 and 17 we have:

$$\frac{Q_1}{K_1 \cdot X_1} = \frac{Q_2}{K_2 \cdot X_2} = \frac{Q_3}{K_3 \cdot X_3} \tag{18}$$

And with some re-arranging:

$$X_i = \left(\frac{Q_i/K_i}{\sum_n Q_i/K_i} \right) \tag{19}$$

Thus for ideal behavior, a simple analytic solution exists which is a function only of the saturation index for each endmember component. With this equation one can calculate the composition of the least soluble solid solution composition given only the composition of the solution and the saturation indices of the endmember components.

For non-ideal behavior, where the activities of the endmember components are related to their mole fractions by equation 10, finding the maximum of the affinity function is more difficult. In this case the derivatives are more complex and a simple relationship such as equation 19 cannot be derived. Instead, we have used a numerical technique known as the SIMPLEX method to find the maximum of the saturation index. The SIMPLEX method is commonly used in linear programming problems to find a maximum or minimum value of a function subject to some linear constraints among the variables. The hypothetical

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solid solution problem is a type of linear programming problem in that the maximum of a function is desired subject to the constraint that for all X_i:

$$0 \leq X_i \leq 1$$

The algorithm of the SIMPLEX method is based on a theorem which states, in general terms, that the maximum for a function will occur at a boundary or an edge of the n-dimensional space that contains all possible solutions of the function. The SIMPLEX algorithm thus evaluates the function only along corners and edges, and uses results obtained at each point to direct further search to the correct region of the set of possible solutions. * Thus the method immediately eliminates most of the possible solutions to the problem and evaluates only relatively few, which greatly speeds the process of finding the solution.

Use of the SIMPLEX method also makes the subroutine HPSAT completely general. Any form of the equation for calculating the activity coefficients for endmember components can be used.

Verification

To check the accuracy of solutions generated by the SIMPLEX algorithm, two independent techniques were used to solve an identical problem and the results compared. In the first case, problems involving ideal solid solutions having a known analytic solution were tried. In this case the analytic solution was compared with the solution determined using the SIMPLEX algorithm. In all of the several dozen test cases, both methods produced identical results.

The second test involved using a separate numerical algorithm, the 'direct search' method. This is one of the simplest methods for finding maxima and minima for a function. With this method, the function is evaluated systematically over some arbitrary grid of possible solutions. For the case of finding the maximum, the function evaluations are compared and the region or regions having the largest values are noted. A smaller grid is then placed around these largest values and a second grid and set of evaluations are made. This process continues until the desired accuracy is achieved (the grid spacing is smaller than the minimum accuracy required). The method is clearly slow because very large numbers of function evaluations must be made, but is so simple that it is reliable, even with extremely complicated functions. One requirement is that the functions are continuous, which is the case for the affinity function for solid solutions. Once again, comparisons of the solutions using SIMPLEX with those determined using the direct search method were identical in each of several dozen test cases.

Limitations

For the case of ideal mixing model, the algorithm employed by HPSAT calculates mole fractions of components to the accuracy of real number division by the host computer. However, solutions for non-ideal solutions obtained using DSIPLX (the subroutine performing the SIMPLEX maximization) are less accurate, particularly for cases where some

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* A good discussion of the SIMPLEX method and simple geometric examples of the approach can be found in chapters 3 and 5 of Anton and Kolman Applied Finite Mathematics Academic Press, New York, 1974.

endmembers are present only in trace amounts. This is because DSIPLX must find the maximum of a function which is a sum of terms, each term of which correspond to each endmember component. If one endmember is dominant (i.e. has a mole fraction near unity), the size of its corresponding term in the function to be maximized is orders of magnitude larger than the terms for the components present in trace quantities. Thus the algorithm has difficulties maximizing the sum since small changes in the amounts of trace constituents may not change the value of the sum to within the limit of real numbers on the computer. This problem is partially overcome by using DOUBLE PRECISION real numbers. However, even so, the algorithm may still fail to converge, or solution oscillate indefinitely in the DSIPLX subroutine, when trace components have mole fractions less than about 10^{-8}. Because of this problem, HPSAT first checks the ideal solution to make sure that the concentrations of all the components are greater than 10^{-8}. If any are less than that amount, they are excluded from the non-ideal solution and the ideal solution is used instead. In the future it may be desirable to replace this ideal solution for trace constituents with Henry's Law type expressions based on experimental data.

Presently, the algorithm in HPSAT only works with solid solutions that mix on one site. As mentioned above, modifications to allow it to work with more complex solid solutions are in progress. Also, analytic solutions for non-ideal cases will be investigated and a NEWTON-RAPHSON technique for solving the problem will be tested. This technique may not be limited at low mole fractions as is the SIMPLEX method.

The approach described here is based on mixing of endmember components. A better approach for more complex phases that mix over multiple sites is the site-mixing model for solid solutions, which calculates thermodynamic properties for a particular composition based on the energetics of ion interactions on specific coordination sites in the crystal lattice. This approach has been used successfully for modeling solid solutions of high-temperature phases such as pyroxenes and garnets. However, applications to low temperature phases such as clays and zeolites is severely limited by a current lack of fundamental thermodynamic data. Also, this approach is necessarily complicated, especially if more than nearest neighbors are considered. However, this approach is preferable to methods that use molecular endmember components because it can correctly take into consideration structural changes and and changes in bonding energies that are necessarily overlooked with the endmember approach. True site mixing models of solid solutions have received some attention in the geochemical literature.[*] However, most models that have been developed for real solid solutions are based on the endmember component approach and therefore most of the data available are of that type.

Additions to the Database

Presently the database contains entries for the following solid solutions: sanidine-albite, biotite, Ca-smectite, Na-smectite, olivine, orthopyroxene, and plagioclase. Of these, only olivine currently has non-ideal mixing parameters. Work is presently underway to enter non-ideal mixing models for the others. Data on the high-temperature pyroxene and garnet solid solutions will also be added. Although not relevant in low-temperature repository conditions, these data will be used to verify the solid solution algorithm of the code.

In addition, a literature search will be carried out for information on solid solutions

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[*] the most recent and comprehensive is that of Helgeson and Agaard (1985)

of clay and zeolite minerals. These phases are necessary for modeling tuff-groundwater interactions. Critically selected models will be incorporated into the code.

And finally, models for trace element partitioning into carbonates, sulfides, oxides, spinels, olivine, and pyroxenes have been formulated by Sverjensky (1985). These models and the supporting database are currently being incorporated into the code. These additions will better enable the code to deal with the solubility limits of metals, including radionuclides, as trace constituents in solid phases.

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